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Removal of TcO_4^- ions from solution: materials and future
outlook

Removal of radioactive pertechnetate from legacy nuclear waste
is an environmental concern. Solid state ion-exchange materials
such as resins and ionic metal–organic frameworks (i-MOFs) can
selectively remove pertechnetate and related ionic oxyanions.

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Removal of TcO_4^- ions from solution: materials and future outlook

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Technetium mainly forms during artificial nuclear fission; it exists primarily as TcO_4^- in nuclear waste, and it is among the most hazardous radiation-derived contaminants because of its long half-life ($t_{1/2} = 2.13 \times 10^5$ years) and environmental mobility. The high water solubility of TcO_4^- (11.3 mol L^{-1} at 20°C) and its ability to readily migrate within the upper layer of the Earth's crust make it particularly hazardous. Several types of materials, namely resins, molecular complexes, layered double hydroxides, and pure inorganic and metal–organic materials, have been shown to be capable of capturing TcO_4^- (or other oxoanions) from solution. In this review, we give a brief description about the types of materials that have been used to capture TcO_4^- and closely related oxyanions so far and discuss the possibility of using metal–organic frameworks (MOFs) as next-generation ion-exchange materials for the stated application. In particular, with the advent of ultra-stable MOF materials, in conjunction with their chemical tunability, MOFs can be applied to capture these oxyanions under real-life conditions.

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Key learning points

- (1) The general idea and associated technical challenges in removing pertechnetate from nuclear waste.
- (2) The urgency in removing TcO_4^- from nuclear waste.
- (3) Capture and separation of TcO_4^- from a chemist's point of view.
- (4) Ionic MOFs (i-MOFs) as ion exchange materials.
- (5) Design principles of i-MOFs for TcO_4^- removal.

1. Introduction

The ion-exchange process is widely applied in many industrial and household applications and is a critical component of our modern lifestyle.¹ In particular, ion exchange is widely used for purification, separation, and decontamination purposes in the food and beverages, chemical, pharmaceutical, water, power, and nuclear industries. Typical commercial ion exchangers are ion-exchange resins, zeolites and clays, which can be either cation exchangers or anion exchangers depending on their chemical structures.^{1,2} The ion-exchange capability and selectivity of an ion-exchange material for a particular process depend on several factors, including but not limited to its chemical structure and the size and charge of the ions. Ion exchange is generally a

reversible (or elutable) process, where the ion exchanger can be readily regenerated with desirable ions by simple washing. In an irreversible (non-elutable) process, a bonding interaction occurs between the target ion and the host material: a typical example is the co-crystallization of the target ion with the host and subsequent precipitation of the new phase out of the solution.^{3,4}

Ion-exchange processes have also found applications in nuclear industries, particularly for radioactive waste disposal applications.^{5–7} These wastes are generated during fuel rod reprocessing, power generation, radiochemical research, and defense related activities. Although the type of waste varies based on its origin and reprocessing technology, ^{99}Tc , an isotope of technetium with a half-life of 213 000 years, is generally one of the significant components within the waste stream. In a mostly aqueous waste stream, ^{99}Tc is present primarily in its most stable oxidation state (vii), as TcO_4^- . TcO_4^- has high environmental mobility and thus poses a real threat to groundwater contamination and aquatic life forms. This threat is particularly significant for legacy waste sites, *i.e.*, geographical sites where radioactive wastes were typically stored due to historic activities

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related to power production and military programs. For example, the Hanford Site in Washington State stores millions of gallons of mixed hazardous wastes and their related radioactive materials for future treatment and subsequent disposal. One of the world's largest environmental cleanup projects is underway at the Hanford site in Washington state. Office of River Protection mission is to safeguard the nuclear waste stored in Hanford's 177 underground tanks, and to manage the waste safely and responsibly until it can be treated in the Waste Treatment and Immobilization Plant for final disposition.

Ion exchange is considered the most viable method to capture TcO_4^- from the bulk waste stream, and different types of materials, such as resins, molecular complexes, and inorganic materials, have been shown to be successful in capturing TcO_4^- under realistic conditions.^{3,4,8,9} Often ReO_4^- , a nonradioactive structural analogue of TcO_4^- , is used to assess the ion-exchange

Table 1 Structural and thermodynamic comparison between ReO_4^- and TcO_4^- .^{3,11}

	ReO_4^-	TcO_4^-
$\text{p}K_a$	-0.28	0.033
Charge/volume ($1/\text{\AA}^3$)	0.048	0.048
DG_{hydr} (kJ mol^{-1})	-330	-251
UV-Vis bands (nm)	230	247, 280
$r(\text{X}-\text{O}/\text{\AA})$ (X = Re, Tc)	1.72-1.73	1.71
$R_{\text{H}_2\text{O}}^a$ (\AA)	2.6	2.5
$Q/S \times 10^{2b}$ (\AA^{-2})	1.2	1.3

^a $R_{\text{H}_2\text{O}}$ = ionic radius in water. ^b Q/S = surface charge density of an ion.

properties, given the difficulty in dealing with radioactive TcO_4^- in a typical laboratory setup (Table 1). In this review, we give a short perspective on TcO_4^- capture from nuclear waste streams using traditional materials such as resins and inorganic ion exchangers.



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Debasis is a postdoctoral associate at the Materials Science group of Pacific Northwest National Laboratory (PNNL), working with Dr Praveen Thallapally. He received his PhD in Inorganic Chemistry under the guidance of Prof. John B. Parise at Stony Brook University, where his research focus was on the synthesis of s-block metal based coordination networks and their characterization. Currently he is working on different aspects of MOFs including noble gas-adsorption and separation, removal of toxic and radioactive ions from solutions and the basic understanding of MOF growth and crystallization.



Dongsang Kim

Dongsang Kim is a lead scientist of the Advanced Waste Glass program at the Pacific Northwest National Laboratory to develop glass property models and glass formulation algorithms for the vitrification of radioactive wastes at the Hanford site for US DOE Office of River Protection. He received his PhD in Materials Science in 1992 at Case Western Reserve University. He also leads fundamental research efforts (i) to understand the mechanism of technetium-99 incorporation into glass during waste vitrification and (ii) to understand the effects of anion species (CrO_4^{2-} , Cl^-) on the solubility of sulfate in waste glass.



Michael J. Schweiger

Michael J Schweiger is a glass scientist and project manager at Pacific Northwest National Laboratory for the past 32 years. More recently his efforts have focused on solving technical problems and development of new approaches related to nuclear waste glass including measurement of solids dissolution within reacting cold cap, determination of solubility of Tc, Re, I and SO_3 in glass, modifying a laboratory scale melter to perform melter tests within the laboratory and resolving issues related to glass additives and melt responses with maximized loading of waste glasses. He also manages projects for the team he works with. Prior to working in the lab, Mike was a K-12 teacher.



Albert A. Kruger

Earning a BS with Honors at Brooklyn College, Albert began a doctoral program at Syracuse University. He moved to the Bell Telephone Laboratory in Murray Hill, then to the Physics & Materials Group of the 3M Central Research Labs in Minnesota as a Group Lead for Fiber Optic and Novel Electrophotography Materials Research and subsequently to the Saint-Gobain Recherche in Aubervilliers France. Albert holds in excess of 30 patents, has authored over 100 scholarly papers including a prestigious Solvay Seminar, and has lectured at the NATO Summer School. Albert is a Full Member of Sigma Xi. Albert is the DOE Glass Scientist.

We also discuss the use of functionalized metal–organic frameworks (MOFs) for ion-exchange applications and their possible use in TcO_4^- capture from nuclear waste streams.

2. Historical perspective

Although trace amounts of technetium are naturally present in the environment because of the spontaneous fission of uranium isotopes, the major source of radioactive ^{99}Tc is the production of weapon-grade plutonium (^{239}Pu) during irradiated uranium fuel element reprocessing.¹⁰

In the United States, most of the high-level radioactive wastes are stored in underground tanks at the Savannah River Site (SRS) in South Carolina and the Hanford site in Washington State. These wastes date back to the Manhattan project of World War II and plutonium production during the Cold War. For example, the Hanford site stores ~ 53 million gallons of radioactive waste in 177 large underground tanks.^{5,7} The U.S. Department of Energy (DOE) is legally responsible for retrieving, immobilizing, and ultimately safely disposing these radioactive wastes. The general strategy for waste treatment is the separation of solid and liquid wastes first by means of gravity. The wastes are then partitioned into high-level and low-activity waste fractions. The smaller volume high-level waste (HLW) fraction is (at SRS) or is planned to be (at the Hanford site) immobilized in a borosilicate glass waste form (a process known as vitrification) suitable for disposal in a geologic repository. The larger volume liquid low-activity waste (LAW), on the other hand, will be treated into a suitable waste form and stored at the respective sites. The LAW at the SRS will be converted to into a cementitious waste form (called Saltstone) while the waste at the Hanford site is planned to be vitrified into a borosilicate glass waste form, similar to that of the HLW form. At the Hanford site, the radioactive waste contains a large amount of ^{99}Tc ($\sim 9 \times 10^2$ TBq or $\sim 2.5 \times 10^4$ Ci or ~ 1500 kg) mostly partitioned into LAW as TcO_4^- , as this is

the most stable form in oxygen saturated solution, although a significant fraction (2% to 25%) of the ^{99}Tc may be present as soluble non-pertechnetate species such as Tc(I) carbonyl compounds.

^{99}Tc (which, along with uranium and plutonium, is insoluble under storage conditions) is one of the most difficult contaminants to address at the DOE Hanford site because of its complex chemical behavior in tank waste and limited incorporation into a glass waste form during high-temperature vitrification processes due to its high volatility. The current strategy to overcome the high volatility issue, which results in low concentrations of Tc incorporated into the final glass product, is to collect and send the off-gas condensates back to vitrification facility to eventually retain $\sim 100\%$ of the Tc in glass. The off-gas stream also includes other volatile species in addition to Tc, such as sulfur and halides that have the negative effect of increasing the volume of waste form to be stored at the disposal site. Therefore, research efforts are in progress to develop technologies that can efficiently manage Tc without recycling the off-gas condensates. One of the promising methods is to capture Tc from the off-gas condensates and to treat the Tc-depleted (completely or partially) off-gas stream into a low-temperature waste form, which avoids concerns of Tc volatility. The resulting Tc-absorbent can either be sent back to the vitrification facility for full incorporation into a glass waste form or remain in the off-gas stream for encapsulation within the aforementioned low-temperature waste form matrix, depending on the chemical and physical properties of the Tc-bearing phase.

It is possible to capture and remove TcO_4^- using a number of processes such as ion exchange, extraction, and precipitation.^{3,4,10,11} Each of these processes has its own advantages and disadvantages, but $^{99}\text{TcO}_4^-$ removal by ion exchange has received the most attention to date because of its ease of implementation and high ^{99}Tc recovery rate.¹⁰ In this regard, over the last few decades, a considerable amount of work has been done on removing ^{99}Tc from Hanford tank wastes in the form of $^{99}\text{TcO}_4^-$ using anion-exchange resins (such as SuperLigTM).^{5,7,12} Although effective removal of TcO_4^- was observed from a simulated nuclear waste stream, there is room for improvement in terms of selectivity and capacity.

3. Materials of interest

Since most of the ^{99}Tc species are present as $^{99}\text{TcO}_4^-$ within the nuclear waste streams, different types of anion-exchanging materials have been used thus far, to test their effectiveness in removing TcO_4^- : ion-exchange resins,⁷ molecular and supra-molecular complexes (e.g., cryptands and calixarenes),¹¹ and different types of inorganic materials (e.g., layered double hydroxides or LDHs).^{8,9,13} Apart from these traditional materials, very limited studies have been carried out on inorganic–organic hybrid materials (also known as metal–organic materials or MOFs).¹⁴ In the next sections, we will briefly describe each type of material used so far for TcO_4^- removal by ion-exchange mechanisms.



Praveen K. Thallapally

Praveen K. Thallapally has been a senior research scientist at the Pacific Northwest National Laboratory since 2006. He obtained his PhD in 2003 from the University of Hyderabad working with Prof. Gautam R. Desiraju in the area of Crystal Engineering of organic and metal organic solids. He moved to the University of Missouri Columbia as a post-doctoral fellow working with Prof. Jerry L. Atwood in the area of supra-molecular chemistry, gas storage

and separation. He leads research efforts in the design of porous materials for energy conversion, separation, and catalysis. He is a board member for Crystal Growth & Design, CrystEngComm and Journal of Coordination Chemistry.

3.1. Ion-exchange resins

Ion-exchange resins are insoluble matrix or support structures fabricated using an organic polymeric substrate.¹⁵ The cross-linked resin polymeric networks are the insoluble phase to which an ion is electrostatically bound. This ion can be exchanged with a solution containing ions of the same charge, the extent of which depends on the concentration of the ion(s) in solution and the affinity of the ion(s) for the insoluble phase relative to the solution phase.¹⁵ The most common ion-exchange resins are based on a polystyrene sulfonate backbone. The resins can be cation or anion exchanging based on the side chain functionalities. Different types of resins have been synthesized based on different polymeric networks and different organic functionalizations (*e.g.*, crown ether, trialkylamine) covalently bound to the polymer.^{7,16} Resins have been used in applications ranging from water softening, environmental remediation, wastewater treatment, chromatography, biomolecular separations, and catalysis.¹⁵ Ion-exchange resins were also used for TcO_4^- removal from alkaline tank wastes at Hanford during the mid-sixties;^{7,10} these include IRA-401, a styrene divinylbenzene copolymer with quaternary ammonium side chains, and others (Fig. 1).⁷ A Tc recovery rate of 70% was achieved in a process where the tank waste was first passed through a bed containing an inorganic ion-exchange material to separate radioactive ^{137}Cs and then through the IRA-401 column. The resin bed approached 50% breakthrough of ^{99}Tc at the end of complete loading of tank waste; this can be modified by changing the column length. The adsorbed TcO_4^- was later recovered using concentrated nitric acid. Since then, the DOE has conducted extensive testing of both commercial and developmental ion-exchange-based organic polymers and

resins to find a suitable material for separating TcO_4^- from nuclear waste streams (Fig. 1). Materials such as Purolite-A-520E (*e.g.*, a macroporous anion exchanger with a trimethylamine group) and Reillex™ HP (*e.g.*, an *n*-butyl derivative of poly-4-vinylpyridine/divinylbenzene), which possess a polymeric matrix with ionic side chains, show high TcO_4^- uptake under realistic conditions (Fig. 1) (distribution coefficient $K_d = 1300 \text{ mL g}^{-1}$ and 1405 mL g^{-1} , respectively).⁷ Although these resins show comparable TcO_4^- uptake, the difference lies mainly in their pretreatment and regeneration strategies. For example, Reillex-HPQ-type resins need to be regenerated by $\text{NaOH}/\text{Sn(II)}$ /ethylene-diamine or strong acid solution, while aqueous biphasic extraction chromatography (ABEC) resins can be regenerated by simple washing with water (Fig. 1).⁷

All these resins described so far are monophasic, *i.e.*, they contain only one type of functional group. Gu and coworkers showed that the use of bifunctional resins (known as RO-02-119), *i.e.*, resins with two different functional groups, can lead to improved selectivity and sorption kinetics for TcO_4^- removal from contaminated groundwater with respect to several benchmarks, including commercially available, mono-functionalized resins such as Purolite A-520E (Fig. 1).¹⁶ A bifunctional resin is composed of two types of quaternary ammonium groups, one with long chains (triethylamine) for higher selectivity for poorly hydrated large anions, and one with shorter chains (trimethylamine) for enhanced kinetics and exchange capacity. The resin was particularly effective for removing low levels of TcO_4^- ($\sim \text{nmol L}^{-1}$) from contaminated groundwater. However, it is reasonable to expect the resin performance to be significantly lower with alkaline nuclear waste, where the amine groups are likely deprotonated.

Among all the resins used so far, SuperLig-639™, a resin consisting of a polystyrene matrix with a crown-ether based organic linker covalently attached, shows the best adsorption-separation capacity under realistic conditions (Fig. 1).⁷ SuperLig-639 was the baseline material for technetium removal from the Hanford tank waste supernatant until Tc(VII) was removed from the Waste Treatment and Immobilization Plant (WTP) flowsheet. SuperLig-639 was chosen because of its high selectivity for TcO_4^- , elutability, and availability in an engineered form that is suitable for use in ion-exchange columns. SuperLig-639 is commercially manufactured by IBC Advanced Technologies (American Fork, Utah). It shows an excellent $^{99}\text{TcO}_4^-$ exchange capability with $\sim 99\%$ removal efficiency from the alkaline waste solution with high $^{99}\text{TcO}_4^-$ content. The removal efficiency is lower ($\leq 86\%$) for waste solutions that also contain significant amounts of non- TcO_4^- ions. The exceptional TcO_4^- efficiency of SuperLig-639 is attributed to the presence of the crown-ether group, which can form an ionic complex with the TcO_4^- counter cation (*e.g.*, Na^+ , K^+).⁷ It was initially postulated that there is an optimal size fit between a crown ether and particular cations. For example, [18]-crown-6 is selective for K^+ , while [21]-crown-7 selectively adsorbs the larger Cs^+ and Rb^+ .¹⁷ However, since these moieties are flexible in nature, it is likely that other factors, such as solvation energies of the respective ions or host-guest interactions, play a role in

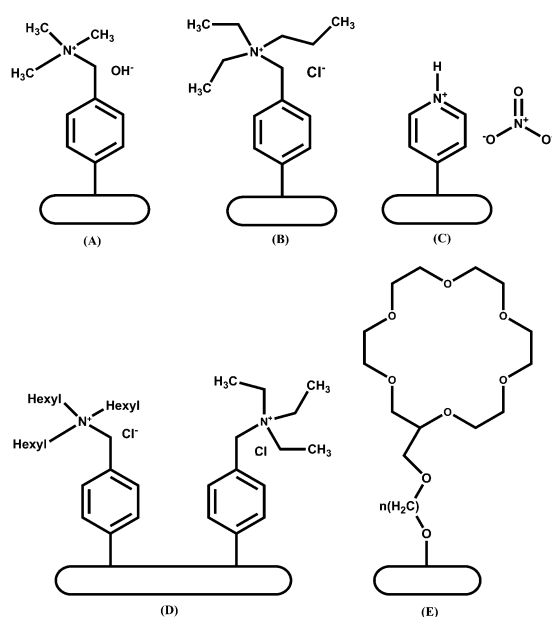


Fig. 1 Pictorial representation of TcO_4^- selective resins: (A) IRA-401, (B) Purolite A-520E, (C) Reillex™-HP, (D) RO-02-119, (E) representative example of a SuperLig™ system on a solid support. 18-crown-6 is chemically attached by a tether to both the linker and the solid support.

the selectivity. Due to an abundance of Na^+ and K^+ in the alkaline waste stream at the Hanford site, TcO_4^- is expected to be present as NaTcO_4 or KTcO_4 species in the solution. Experiments have shown that Na^+ or K^+ ions (with TcO_4^- counter ions) can readily form complexes with the crown ether, thereby removing the TcO_4^- from the waste stream.⁷ As the crown-ether functionalized resins have overwhelming selectivity for Na/KTcO_4 species over other salts such as Na-KNO_3 , no expensive pre-treatment is necessary. The TcO_4^- can then be recovered using an inexpensive stripping process (*i.e.*, elutable option), regenerating the crown ether for multiple cycles without significant generation of secondary waste. Although SuperLig-639 has shown extremely high TcO_4^- capacity, the drawbacks of SuperLig-639 include lower selectivity in the presence of nitrate anions and the cost of producing a large quantity due to the sole source of SuperLig-639.

3.2. Molecular and supramolecular receptors

Supramolecular chemistry generally involves the chemistry of molecular assemblies and intermolecular bonds.^{11,17,18} Since the inception of supramolecular assemblies, anion recognition and separation by supramolecular (and molecular) receptors has developed into a vibrant area of research.^{3,11,18,19}

The anion recognition and successive separation generally follows a solvent extraction procedure, rather than a direct ion-exchange process as in the case of solid-state materials.^{3,11} As a result, the solvation energies of anions in their respective extraction solvents become important. The trend is generally monotonous (Hofmeister bias) with respect to their partitioning behavior between aqueous and organic phases.³ Thus, while the extraction of strongly hydrophilic anions, such as phosphate and sulfate, from water to the organic solvent is challenging, charge-diffuse anions, such as ClO_4^- and TcO_4^- , are much easier to remove from water by using relatively hydrophobic receptors.¹⁷ This is possible because in the latter case, the anions have less hydration energy due to their smaller charge/radius ratio (Table 1), resulting in a lower energy penalty for extraction. Organic hosts can be either cation or anion selective, based on their chemical nature. An alternative approach to the anion recognition is the selective entrapment of counter cations. Because the cations possess lower solvation energy than anions, they are easier to trap, as the related energy penalty is comparatively lower.¹⁷

Anion (or cation) recognition also depends on the charge of the host under the experimental conditions.^{3,11} Typically, neutral anion receptors incorporate strong, multiple hydrogen bond donor groups such as urea. These groups act both as binding sites and as the backbone of the receptor system.³ It is to be remembered that since the receptor is neutral, it will not only bind an anion, but will also bind its counter cations. As a result, the type and solvation characteristics of the counter cation can play an important role in the overall host selectivity. To overcome this issue, the system can be deliberately modified with 'noncompeting' ions (*e.g.*, tetraalkylammonium cations or tetraarylborate anions).^{3,11} In these cases, the charged receptor only interacts with the targeted anions of cations, giving rise to a higher selectivity or binding constant. However, in reality,

noncompetitive counter ions, such as those mentioned above, are not generally encountered and significant inter-ion competition is observed. The most obvious way to bind an anion is to design a host that contains positive electrostatic charge. However, most of the anions only exist in a narrow pH range and the cationic sites of the hosts may not be fully protonated at that pH value.^{11,17}

There are two major classes of hosts: acyclic (podands) and cyclic (macrocycles, macrobicycles, or macrotricycles).¹⁷ Podands are linear or branched chain species with two or more sets of guest-binding functional groups. These functional groups are positioned on the spacer unit to chelate to a target guest species, maximizing guest affinity. The chemical functionalities generally have a high degree of flexibility, and often upon binding with the target guest species, a conformation change occurs to form a stable host-guest species. Such host flexibility is thus considered of key importance, similar to biological systems (*e.g.*, proteins), where the recognition of a substrate results in conformational changes that may be of major significance.¹⁷ The simplest of acyclic hosts are positively charged organic linkers, forming salts with tetrahedral oxyanions (*e.g.*, ReO_4^- , TcO_4^-) through H-bonding donor centers.¹¹ In one such example, Jurisson and coworkers found that phosphinimine complexes of ReO_4^- and TcO_4^- exist as stable ion pairs, namely $[\text{Ph}_3\text{P}=\text{NH}_3^+][\text{XO}_4^-]$ ($\text{X} = \text{Tc}, \text{Re}$) in aqueous and organic solutions (Fig. 2).²⁰ The phosphiniminium ion of the starting salt is not stable in solution and undergoes hydrolysis to first form phosphinimine and then phosphine oxide.

Acyclic hosts exhibit lower binding constants than their cyclic analogues because of their difference in pre-organization.¹⁷ Cyclic receptors, on the contrary, have their binding sites positioned in a pre-organized closed-ring format, which leads to the formation of thermodynamically stable complexes as less conformational changes are required upon binding.¹⁷ Furthermore, these cage receptors can provide a well-defined three-dimensional (3D) cavity with a functionalized pore surface, ensuring selective binding. However, these organic cages with specific functionalities are often hard to synthesize, involving many steps and

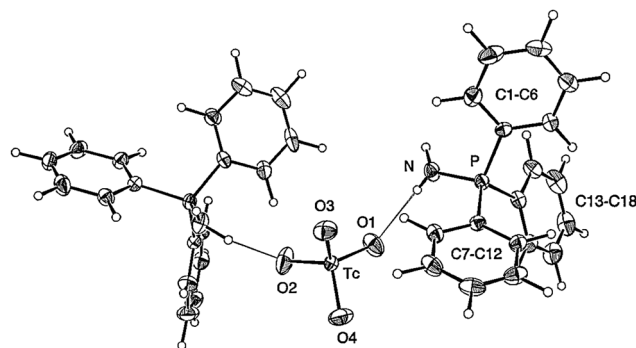


Fig. 2 ORTEP representation of $[\text{Ph}_3\text{P}=\text{NH}_2^+][\text{TcO}_4^-]$. One anion and two cations are shown, illustrating the intricate hydrogen bonding network between the phosphonium proton and the pertechnetate oxygen atoms in the crystal lattice. Reprinted from Permission from ref. 20. Copyright 1999 Springer.

tedious purification processes. To overcome these challenges, self-assemblies are often considered a more practical approach: in one step, simple building units come together to form complex architecture.³ A special case of such self-assembly is co-crystallization, where the target anions crystallize with the receptors to form a solid phase. The counter cation, included in the crystal structure for charge balancing purposes, can also play a part in selectivity (*e.g.*, complete rejection of anions with different charges). Moyer, Custelcean and coworkers reported the formation of an exclusive class of crystalline capsules self-assembled from tripodal TRENtris-urea (TTU) ligands (TREN = tris(2-aminoethyl)amine) and their thiourea analogues.^{3,4} These capsules can selectively adsorb cations such as Na^+ and Cs^+ by means of intramolecular H-bonding, whereas the counter anions (*i.e.*, ReO_4^- , TcO_4^-) remain with the host for charge balancing. Similar concepts of indirect TcO_4^- capture were also applied using other cation-selective hosts, such as crown ethers, calixarenes, and cryptands.¹⁷ For example, the crown-ether moieties in SuperLig-639 were used to indirectly remove TcO_4^- from aqueous solution. While SuperLig-639 represents an example of a solid-state ion-exchange material, crown-ether based host systems have been used for TcO_4^- extraction as well. Similarly,

efficient removal of TcO_4^- species from alkaline wastewater was achieved in the SRTALK process, where bis-4,4'(5')[(*tert*-butyl)-cyclohexano]-18-crown-6 was used as the crown-ether source (Fig. 3).²¹ The crown ether is present in a mixture of extractants, tributyl phosphate, and Isopar/L. As the process works under alkaline conditions, extraction can be directly applied to the waste tank supernatant without any need for acidification. The mechanism of extraction is similar to what was observed in the case of SuperLig-639, *i.e.*, the crown ether directly complexes and extracts metal cations such as Na^+ , K^+ and Sr^{2+} , and to preserve charge neutrality, TcO_4^- is co-extracted.

In contrast to the types of receptors discussed above, a ditopic receptor can bind to both cations and anions by exhibiting cooperative behavior. Beer and coworkers reported a crown-ether based receptor, tripodal tris(amido-benzo[15]crown-5) that can bind (and extract) with both Na^+ and TcO_4^- in the presence of excess Cl^- under conditions that mimic the aqueous nuclear waste stream (Fig. 4).²² It was postulated that as the Na^+ ion form complexes with the crown ether, it leads to a conformational change of the crown ether. This conformational change and associated “size match” are beneficial for the adsorption of TcO_4^- (or ReO_4^-) over Cl^- .

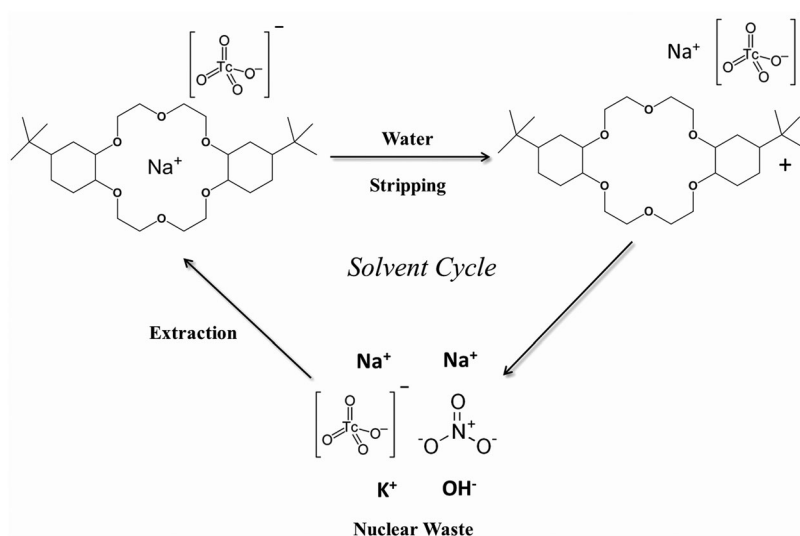


Fig. 3 Schematic diagram of the SRTALK process using a crown-ether based extractant.

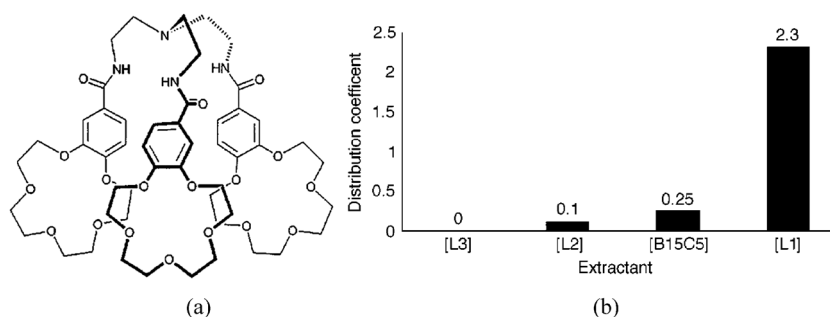


Fig. 4 (a) Schematic of the crown-ether receptor, tris(amido-benzo[15]crown-5) (L1); (b) distribution coefficient for TcO_4^- extraction by the amino constituents of L1. B15C5 represents the free crown ether. Reprinted with permission from ref. 22. Copyright 1999. Royal Society of Chemistry.

Cryptands and calixarenes are other two organic cage-type receptors that can indirectly capture anions by means of cation capture. Cryptands offer better selectivity and binding strength for Na^+ and K^+ owing to their denser chemical connectivity and have the unique capability to transfer ions from one solvent to another during the extraction process. However, they are prohibitively expensive and often difficult to synthesize in phase-pure form. Calixarenes are bowl-shaped cyclic hosts that are synthesized by condensation reactions between a *p*-substituted phenol and formaldehyde.¹⁷ The atom numbers of the cycle (and thus the respective diameter) can be varied by changing reaction conditions such as the reactant ratio and temperature. Among different types of calixarene molecules, *p*-*t*-butylcalix[*n*]arenes (where *n* = the number of phenol-derived repeat units, *n* = 4, 6, 8) are the most well studied because of the ease of functionalization of the top and bottom (top: location of the *t*-butyl-phenolic substituent, bottom: hydroxyl groups), and by doing so different types of cyclic hosts can be synthesized to capture different types of ions.¹⁷

A crown-ether functionalized calixarene, namely calix[4]arene-bis-crown-6, was used to co-extract Cs^+ and TcO_4^- from basic nuclear waste within the scope of the Actinex program (commissioned by the French Alternative Energies and Atomic Energy Commission).²³ X-ray single crystal diffraction and molecular modeling studies were used to reveal the ion-framework bonding interaction. A cesium ion was located within a crown-ether loop, where it forms a weak coordination interaction with crown-ether oxygen atoms. The cesium ion is also involved in bonding interaction with water and nitrate ions from the nuclear waste solution. A second step involving separation of cesium and TcO_4^- was also attempted using the same host molecules, but it proved difficult to achieve because of the ineffectiveness of TcO_4^- stripping using dilute HNO_3 solution.

Apart from such organic functionalization, a number of organometallic bowl-shaped anionic hosts have been prepared based on Ru(II), Rh(III) and Ir(III) complexes with calix[*n*]arene (*n* = 4, 5) and cyclotrimeratrylene (CTV) (Fig. 5).^{24,25} These metalated macrocycles possess positive charges owing to the presence of positively charged metal clusters, and thus can intrinsically act as anionic receptor molecules. CTV is a bowl-shaped molecule with a shallow cavity and is highly pre-organized because of the conformation preference of the associated aryl rings.¹⁷ The incorporation of organometallic moieties around the exterior of the CTV molecule forms a highly electron-deficient cavity, resulting in strong, cooperative electrostatic host-anion interactions, giving rise to very short host-anion contacts in the solid state.²⁴ For example, the bimetallic ruthenium based host, $[(\text{Ru}(\eta^6\text{-}4\text{MeC}_6\text{H}_4\text{CHMe}_2))_2(\eta^6\text{-}\eta^6\text{-CTV})]^{4+}$ shows a specific affinity toward large tetrahedral cations and can selectively extract both $^{99}\text{TcO}_4^-$ and ReO_4^- from aqueous solution, even in the presence of a large excess of Cl^- , CF_3SO_3^- , NO_3^- , SO_4^{2-} , and to some extent ClO_4^- .²⁴ The extraction studies were conducted using a biphasic system composed of nitromethane and 0.9% aqueous saline, where the host material stayed in the organic phase and acted as a phase transfer agent for anions being extracted from the aqueous phase. The order of selectivity

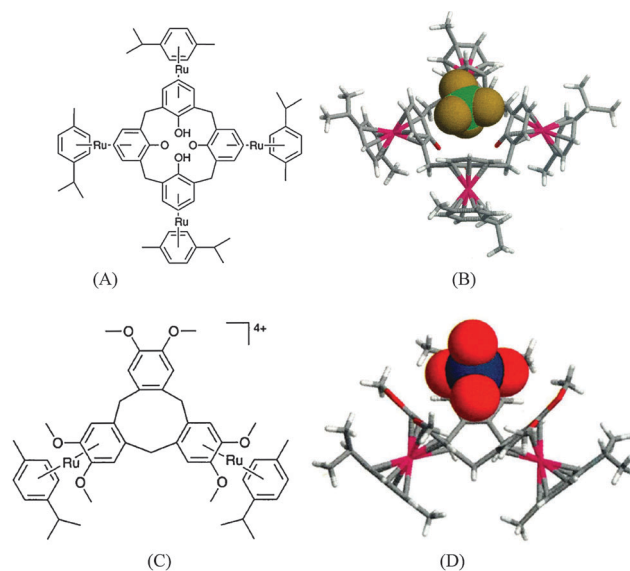


Fig. 5 (A) Ru complex of calix[4]arene; (B) X-ray crystal structure of the tetrametallic host $[\text{Ru}(\eta^6\text{-}(p\text{-MeC}_6\text{H}_4\text{CHMe}_2))_4(\text{calix[4]arene-2H})]^{6+}$ showing the included BF_4^- (C) schematic diagram of $[(\text{Ru}(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2))_2(\eta^6\text{-}\eta^6\text{-CTV})]^{4+}$ (D) crystal structure of the ReO_4^- complex of $[(\text{Ru}(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2))_2(\eta^6\text{-}\eta^6\text{-CTV})]^{4+}$. Reprinted with permission from ref. 24. Copyright 1996. Royal Society of Chemistry.

for large oxanions is as follows: $\text{TcO}_4^- \geq \text{ReO}_4^- > \text{ClO}_4^- \gg \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. Although all these supramolecular complexes show high degrees of selectivity for TcO_4^- during the extraction process, these processes are generally carried out in pure organic solvents, in mixtures of organic solvents, or in water-organic mixtures. For a “real-life” application to succeed, a pure water system is overwhelmingly preferable. Alberto and coworkers reported the binding properties of ReO_4^- and TcO_4^- with azacryptands (e.g., aza functionalized cryptands) in pure water (Fig. 6).²⁶ The binding occurs at acidic pH (pH = 2), where the amine groups of the azacryptands are present in protonated form. The receptor has an overall positive charge of +6.

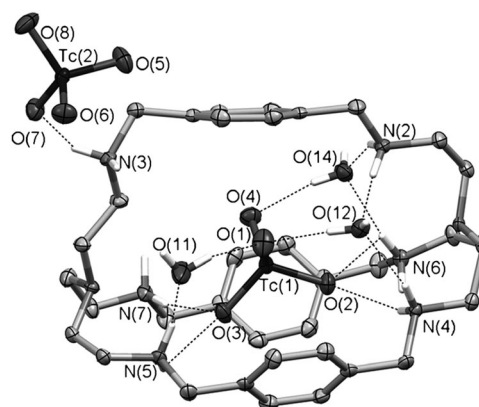


Fig. 6 View of the azacryptand- TcO_4^- interaction. Only $^{99}\text{TcO}_4^-$ anions and the water molecules involved in the interaction with the receptor are shown. Atoms are drawn as ORTEP ellipsoids (50% probability level). Reprinted with permission from ref. 26. Copyright 2012, Wiley-VCH.

Complementary physical studies such as proton nuclear magnetic resonance (NMR), isothermal titration calorimetry, and single crystal X-ray diffraction (XRD) were conducted on the system to understand the origin of TcO_4^- (and ReO_4^-) selectivity over other common anions such as NO_3^- and Cl^- . It was found that the large TcO_4^- selectivity originates from the formation of a 1:1 adduct under experimental conditions: one TcO_4^- molecule present within the cavity interacts with the host molecule through intramolecular H-bonding. The same group of authors later incorporated a fluorescent unit in the azacryptand system.²⁷ The recognition of different anions (or analytes) by fluorescence quenching (or enhancement) is a reliable technique: they are technology friendly, easy to integrate to the existing infrastructure, have high sensitivity, and can selectively identify targeted anions. The system can selectively recognize and sense the TcO_4^- anion at mmol concentration. At acidic pH, where the cage is in the hexaprotonated form, TcO_4^- molecules are recognized by fluorescence quenching. Notably, common anions such as Cl^- , NO_3^- , and SO_4^{2-} do not have any effect on the fluorescence behavior of the complex; this provides an example of TcO_4^- recognition in aqueous solution using optical methods.

To date, molecular and supramolecular complexes have been the most extensively studied materials for TcO_4^- (and related oxanions) capture, often showing excellent properties. However, several factors need to be considered before comparing these class of materials with others, including expensive starting materials and time-consuming multi-step synthesis. Solvent extraction, which is almost universally used for these materials for TcO_4^- abstraction, is a complicated process to implement for large-scale separation.

3.3. Dendrimers

Dendrimers are repetitively branched molecules, typically centered on a core chemical moiety, forming highly symmetric, morphologically spherical compounds.^{28–30} The properties of dendrimers are dominated by the functional groups on the dendrimeric surface. The presence of suitable functional groups can therefore, in theory, be used for TcO_4^- adsorption

from a waste stream. Vogtle and coworkers reported a series of urea-functionalized dendrimers that can effectively bind with TcO_4^- at lower pH (<7) (Fig. 7).³⁰ These dendrimers possess $-\text{NH}_2$ groups on the surface, which were expected to be protonated ($\sim 50\%$ of sites) at physiological pH and were believed to be the primary sites where TcO_4^- is adsorbed. This is evident from the fact that at lower pH, more TcO_4^- is adsorbed than at higher pH due to the presence of a greater number of NH_3^+ sites. Furthermore, Vogtle and coworkers introduced methyl orange units at the periphery of the dendrimers to enhance the pH sensitivity of their system.²⁹ The extractability of the TcO_4^- from the aqueous system to a chloroform system is low below pH 4.5, probably because of the high level of electrostatic repulsion at the positively charged periphery. However, the percentage extraction increases sharply at pH > 4.5 , which is also accompanied by a color change. The stoichiometric ratio of the dendrimer to TcO_4^- was found to be 1:4 under some of these conditions. In a subsequent study by the same authors, dendrimers functionalized with crown ethers were prepared in order to extract NaTcO_4 from an aqueous phase.²⁸ The pH of the aqueous solution was controlled using Tris-HCl buffer. It was found that the maximum extraction (or adsorption efficiency) was obtained at pH 5.4, where the majority of the tertiary amine groups are presumably protonated. However at this pH, crown ethers are not present in protonated form (they are present in fully protonated form at pH ~ 12) and thus are not expected to be involved in TcO_4^- extraction. The TcO_4^- extraction and binding sites are postulated to be the tertiary amine groups within the main framework. Although no competitive ion adsorption studies have been done, since an excess of Cl^- ions is present in the system, it is safe to say that these materials are selective for TcO_4^- over Cl^- .

Dendrimers represent an intriguing class of systems; however there are several roadblocks ahead for any practical application of these materials, including the cost and stability of materials. Furthermore, the mechanism of adsorption is by solvent extraction, which can create issues such as generation

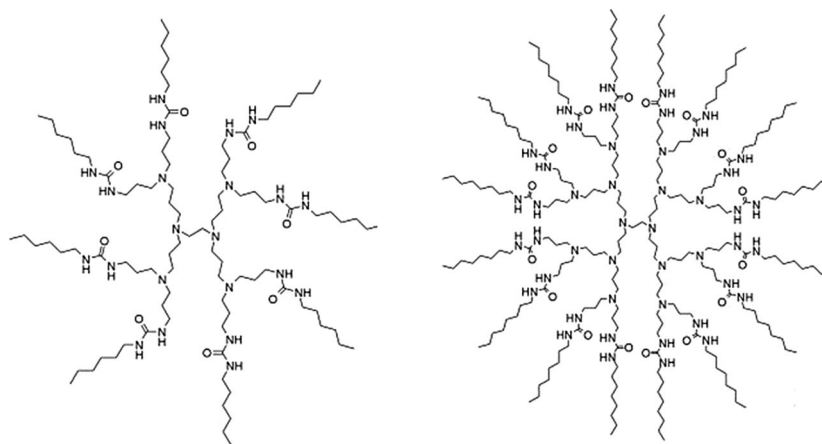


Fig. 7 Representative examples of urea-functionalized dendrimers. Reprinted with permission from ref. 29. Copyright 2001. American Chemical Society.

of a large volume of organic waste, especially in a radiological setting.

3.4. Inorganic materials

For over a century now, inorganic materials such as aluminosilicate zeolites and LDHs have been known for their ion exchanging properties.^{2,13} While zeolites possess aluminosilicate framework-based porous structures that can accommodate a wide variety of cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and others, LDHs are formed by positively charged layers with weakly bound, charge balancing anions (e.g., Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , and SeO_4^{2-}) located in the interlayer region.¹³ The difference in the natures of the extra-framework ions in zeolites and LDHs leads to differences in their exchange properties and therefore their applications. For example, zeolites have been used extensively as ion-exchange materials in water softening (e.g., laundry detergents) by means of the removal of “hard” ions from water. Similarly, LDHs are used for trapping negatively charged ions of various shapes and sizes (e.g., chromate, phosphate, arsenate) from contaminated waters. Several groups have so far reported the application of materials with LDH-type structures for the removal of TcO_4^- or related oxyanions from water by means of anion-exchange mechanisms.¹³ The extra-framework ion-exchange mechanism works by a single mechanism or a combination of multiple mechanisms, namely surface adsorption and interlayer anion exchange.¹³ Surface adsorption involves the attachment of an exchanging ion to the surfaces of the LDHs, forming a molecular or an atomic film on top of the LDH material. The interlayer ion-exchange process involves the exchange of interlayer ions and is mainly influenced by the nature of the charge balancing anions in the interlayer and the layer charge density. Ion exchange reaches its maximum when the interlayer region is big enough to efficiently fit the exchanging anion during the ion-exchange process. Kang and coworkers reported successful TcO_4^- and ReO_4^- exchange with a Mg–Al LDH in both as-synthesized and calcinated forms.³¹ As expected, the calcinated LDH shows a comparatively higher uptake than the non-calcinated version, due to the removal of strongly bound carbonate ions from the interlayer during heating and their subsequent replacement with readily exchangeable hydroxyl groups during rehydration. Wang and coworkers showed that the TcO_4^- sorption capability of an LDH-type material can be greatly enhanced by appropriate manipulation of the composition and structure of materials.³² The adsorption on uncalcinated LDHs was correlated with the basal spacing (d_{003}) of the materials, which increases with a decrease in radii of both divalent and trivalent cations. Sorption occurs at the edge sites of the LDH layers and it reaches a maximum when the layer spacing is just large enough for a TcO_4^- ion to fit inside a cage space among the three adjacent octahedral of metal hydroxide at the edge. Apart from these intrinsic structural features, crystallinity of the solid-state materials also affects adsorption. According to the authors, for a given set of metal cations and interlayer ions, the most crystalline LDH material was obtained with a M(II)/M(III) ratio of 3 : 1, and the Ni–Al–LDH system showed the best TcO_4^- sorption capability among all the LDHs tested.

As mentioned above, the interlayer anions play a major role in determining the total capacity, and materials containing NO_3^- exhibit a higher TcO_4^- (K_d of 1390 mL g^{-1} vs. 209 mL g^{-1}) capture ability than material containing CO_3^{2-} . The reason for the fivefold decrease in adsorption capacity is the thermodynamic stability of the LDHs that contain CO_3^{2-} , owing to strong interlayer binding of CO_3^{2-} .

In essence, although LDHs represent a viable, easy to synthesize system for TcO_4^- removal, there are major challenges to address including (a) de-intercalation in the presence of common anions such as carbonates, (b) low selectivity in the presence of common interfering anions such as chloride and nitrate, (c) the need for calcination before ion exchange and (d) difficulty in recovery and reuse.

Nanostructured chalcogels (e.g., chalcogen-based highly porous semisolids or aerogels) are another class of solid-state materials that have shown significant TcO_4^- uptake at low concentration (10^{-5} M).³³ The total uptake ranges between 57.3 and 98.0%, with PtGe_2S_5 showing the highest uptake among all the chalcogels. Interestingly, the TcO_4^- uptake capacity remains similar for these materials at different pH levels, suggesting a different mechanism of uptake than a traditional ion-exchange mechanism. The sorption studies were only performed at low concentration, so although they show the efficiency of these materials for TcO_4^- removal from solution, uptake selectivity in the presence of other ions, which is crucial for any practical applications, was not studied.

In this regard, Albrecht-Schmitt and coworkers reported a thorium based material, NDTB-1 (NDTB = Notre Dame thorium borate-1) of formula $[\text{ThB}_5\text{O}_6(\text{OH})_6][\text{BO}(\text{OH})_2] \cdot 2.5\text{H}_2\text{O}$, which shows excellent TcO_4^- removal efficiency from water (Fig. 8).^{8,9} NDTB-1 forms a porous supertetrahedral 3D framework structure, where the basic building units are twelve coordinated Th^{4+} ions surrounded by BO_3 and BO_4 anions.⁸ The borate anions further polymerize to form $\text{B}_{10}\text{O}_{24}$ clusters. The bridging of thorium centers with borate clusters creates a supertetrahedral framework, with a system of channels and cages. The charge balancing H_2BO_3^- anions are present within these channels. The extra-framework, weakly bound H_2BO_3^- anions can readily hydrolyze back to H_3BO_3 at a wide range of pH levels owing to the weak acidity of boric acid (dissociation constant $\text{p}K_{\text{a}1} = 9.23$). As a result, other anions can readily get inside the channel of NDTB-1 for charge balancing. Moreover, the channels form a vast intersecting network system, which facilitates anion transport throughout the system. The cavities, formed at the intersections of channels, are also postulated to be capable of trapping anions of suitable size and charge. Therefore, while smaller anions can freely move through the channel, the larger anions are not able to enter the channel, leading to the material's selective behavior. NDTB-1 shows fast and reversible single-crystal–single-crystal (SC–SC) transformation with a variety of common anions such as Cl^- , Br^- , NO_3^- , IO_3^- , ClO_4^- , MnO_4^- , and CrO_4^{2-} .^{8,9} The material shows selective capture of TcO_4^- in the presence of even a large excess of common anions such as Cl^- and NO_3^- . The mechanism of TcO_4^- selectivity was revealed using methods such as detailed competing anion-exchange studies

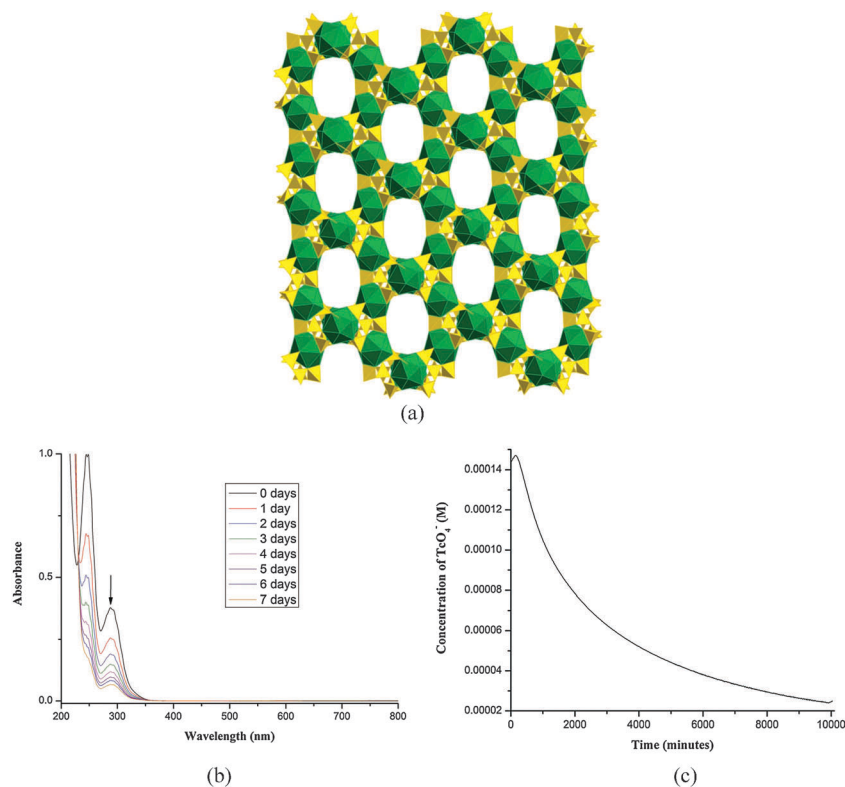


Fig. 8 (a) A view of the supertetrahedral framework structure of NDTB-1 with channels along cubic [110] directions; (b) UV-Vis spectra of TcO_4^- solution exchanged with NDTB-1; (c) plot of TcO_4^- concentration as a function of exchange time. Reprinted with permission from ref. 9. Copyright 2012, Wiley-VCH.

using anions of different charge and size and magic-angle spinning (MAS) NMR spectroscopy.⁹ The selectivity originates from the ability of NDTB-1 to trap TcO_4^- within cavities, whereas other anions remain mobile within the channels of the materials. The anion-exchange capacity of NDTB-1 was found to be 162.2 mg g^{-1} with a second-order exchange kinetics (rate constant $K = 0.059 \text{ s}^{-1} \text{ M}^{-1}$). Interestingly, the TcO_4^- can be reversibly exchanged in NDTB-1 with higher-charged anions of similar sizes, such as PO_4^{3-} and SeO_4^{2-} , and therefore the material can be easily recycled and reused. Although NDTB-1 shows moderate uptake capacity, and more importantly selectivity for TcO_4^- , the radioactive nature of the thorium atom poses a significant barrier for any future applications of this material.

Several different types of mineral systems were evaluated for TcO_4^- removal from nuclear waste, where the primary means of Tc removal is the reduction of Tc(VII) species to Tc(IV) species under anaerobic conditions.³⁴ For example, investigations have been conducted using zerovalent iron and minerals with Fe(II) metal centers under anaerobic conditions, by reducing the Tc(VII) of TcO_4^- to Tc(IV) to form insoluble (and thus immobile) TcO_2 species.³⁴ Among different Fe(II) minerals, magnetite exhibits the highest efficiency for the reduction of Tc(VII) over other Fe(II) minerals such as hornblende and chlorite. The superior reduction capacity of magnetite was attributed to its low band gap and ability to adsorb TcO_4^- by a ligand exchange mechanism. Apart from these solid-state minerals, soluble

Fe(II) complexes can reduce Tc(VII) to Tc(IV) as well, although the lower reduction efficiency of these systems may be too low to be of practical use in controlling TcO_4^- mobility.³⁵

Although they do not fall under inorganic systems, it is relevant to discuss in this section several types of microbes that have been shown to be capable of removing TcO_4^- from solution, by either indirect (*e.g.*, chemical) or direct (*e.g.*, enzymatic) reduction routes.^{35,36} These microbes are either sulfate reducing or iron reducing in nature. For sulfate-reducing microbes, apart from direct enzymatic pathways in some cases, Tc reduction is mediated by an indirect mechanism through metal-sulfide bond formation.³⁶ The reduced Tc(IV) is chemically adsorbed on the surface of the high surface area ($400\text{--}500 \text{ m}^2 \text{ g}^{-1}$) metal sulfide, resulting in rapid and significant TcO_4^- uptake. Similarly, Fe(III) -reducing bacteria can immobilize Tc by a reductive mechanism *via* enzymatically or microbially generated Fe(II) species.³⁵ Although these systems have shown significant and fast immobilization of TcO_4^- species under anaerobic conditions, the presence of a significant amount of dissolved O_2 in the nuclear waste streams needs to be addressed before any practical application is realized.

Finally, even though solid-state materials such as LDHs and NDTB-1 have superior thermochemical stability and are cost effective, most, if not all, have marginal TcO_4^- capacity (and selectivity), which is important for bulk TcO_4^- removal from a nuclear waste stream.

3.5. Porous organic materials

Porous organic materials include materials such as covalent organic frameworks (COFs), covalent organic polymers (COPs) and porous organic polymers (POPs).³⁷ These permanently porous, crystalline materials are formed by molecular building blocks, linked to each other by strong covalent bonds. This is in stark contrast with MOF-based materials where the building units (such as secondary building units or SBUs) are connected to each other by organic linkers, though by comparatively weaker coordination bonding.³⁷ Owing to the presence of strong covalent linkage, these materials generally have better thermochemical stability than MOFs. The surfaces of these materials can be functionalized to form a new generation of ion-exchange materials with high selectivity and uptake capacity. Indeed, Ma and coworkers functionalized a high surface area ($\sim 4100 \text{ m}^2 \text{ g}^{-1}$) and chemically robust POP, called PAF-1, with thiol groups to use it as an effective “getter” for mercury ions from water even at a parts-per-billion level (Fig. 9).³⁸ The thiol groups are chemically attached to the PAF-1 surface, and the surface chemistry of PAF-1 (or other POP materials of similar type) may allow the attachment of other types of groups (*e.g.*, tertiary amines), with high selectivity toward oxyanions such as TcO_4^- , ReO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and MnO_4^- from aqueous media. So far, no anion-exchange studies have been reported on these materials. We believe that by appropriate functionalization, these materials can exhibit substantial adsorption of oxyanions (*e.g.*, TcO_4^- , ReO_4^-) from aqueous solutions. The drawback of these materials lies in their expensive multi-step synthesis process, which should be streamlined before any practical applications using these materials are feasible.

3.6. MOFs as ion-exchange materials-where do we stand?

MOFs or porous coordination polymers (PCPs) are a new class of permanently porous materials; they are formed by infinite arrays of metal ions, connected by functionalized organic linkers, forming chains, layers, or 3D frameworks.³⁹ MOFs or PCPs are generally synthesized under mild solvo/hydrothermal conditions by directed assembly of prefabricated SBUs in the form of inorganic and organic moieties. The coordination modes of the SBUs and the geometry of the organic linkers,

along with the synthetic conditions, are known factors that govern the underlying topology of the resultant structure. MOFs offer advantages over other types of porous materials (*e.g.*, zeolites, activated carbons), where their hybrid nature and synthetic modularity permit a “design” approach to target novel materials with diverse chemical compositions, pore sizes and chemical and thermal stability.³⁹ To date, MOFs have shown to be useful in numerous applications, including but not limited to gas storage and separation, catalysis, and sensing.³⁹ They generally possess neutral frameworks, where the positively charged metal-based SBUs or PBUs (primary building units) are charge balanced by the negatively charged organic linkers.³⁹ However, a number of MOFs are known that possess an ionic framework (i-MOFs) due to factors such as the presence of extra-framework ions, ionic side chains or simply stoichiometric imbalance between metal centers and organic linkers.^{4,40} The most common cause so far is the presence of extra-framework ions in the cavities or pores of MOFs, resulting either from the counter ions of the reactants or from breakdown of the solvents under the given reaction conditions. Although a wide range of metal ions and functionalized organic linkers are utilized to form MOFs, giving rise to unprecedented structural diversity, the poor thermochemical stability of many of these materials under realistic ion-exchange conditions poses inherent challenges for successful implementation of a MOF-material-based ion exchange for practical applications. Nevertheless, a number of i-MOFs are shown to be capable of undergoing ion exchange without breakdown of their parent structure.⁴ The mechanism of ion exchange in MOFs can vary depending on the nature of the exchange sites within the MOFs (or coordination polymers), ranging from a diffusion controlled solid-state exchange mechanism, as observed in ion-exchange resins or zeolites, to solvent mediated dissolution and recrystallization of MOFs.^{2,4} Apart from basic ion-exchange capabilities, selective ion exchange is another important parameter to be considered for any practical ion-exchange application of MOFs. The ion selectivity in a particular MOF-based ion exchanger may arise from a single mechanism or a combination of mechanisms, such as size exclusion or selective binding within the pores or channels of MOFs. For example, selectivity based on size exclusion occurs when the ions are too large to fit into the pores/channels of the MOF materials, while the preferential

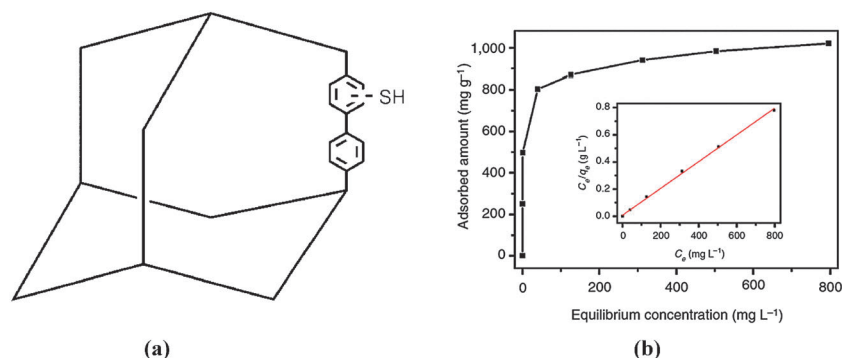


Fig. 9 (a) Schematic diagram of PAF-1-SH; (b) Hg(II) adsorption isotherm for PAF-1-SH. Inset data show the linear regression by fitting the equilibrium adsorption data using the Langmuir adsorption method. Reprinted with permission from ref. 38. Copyright 2014, Nature Publishing Group.

binding of one ion over others within MOFs is due to electronic interactions (*e.g.*, open metal sites). In general, ion exchange in MOFs is often the result of van der Waals or long-range electrostatic interactions, where the exchange selectivity is mainly controlled by solvation-desolvation behavior of the ions in the bulk solution and inside the pores of MOFs. Nevertheless, several studies on ion exchange in MOF-based materials have been reported in the literature, including a number of reviews, and we will briefly discuss some of the representative examples to give readers some perspective on anion exchange in MOFs to date.⁴ The very first ion-exchange study on a coordination polymer (of which MOFs are a subclass) was reported by Robson and Hoskins in 1990, where a copper based 3D coordination polymer was synthesized with diamondoid topology, composed of larger pores filled with a disordered solvent and BF_4^- anions.⁴¹ The anion was shown to be readily exchanged with PF_6^- without much emphasis on the kinetics and selectivity of the ion exchange. Several years later, Yaghi and coworkers reported an example of anion exchange in a silver based 3D coordination polymer by a metal coordination mechanism: the as-synthesized network possesses weakly bound NO_3^- anions with Ag metal centers, which can be reversibly exchanged with anions such as PF_6^- , MoO_4^- , BF_4^- , and SO_4^{2-} .⁴² However since no competing anion-exchange study or structural characterization was carried out on the different ion-exchanged forms, it was difficult to judge whether the exchanged anions have the same types of interactions with the pore surfaces, given the wide difference in their respective electronic and steric natures. Since then several hundred examples of MOF-based ion-exchange materials have been reported. Because of space limitations, we will only briefly discuss the ion-exchange (capture) properties of a few thermochemically stable MOFs from the University of Oslo (UIO) series.^{43–45}

Stock's and Lin's groups have reported examples of ion capture from solution by using functionalized UIO-series MOFs.^{43,44} In those cases, the functionalized side chains are involved in covalent bonding interactions with metal ions in the solution, facilitating the removal of particular ions from solution. The work shows that by incorporating specific functional groups at the core of a framework, it is possible to selectively remove ions (both cations and anions, based on the functional group) from solution.

Stock and coworkers reported on thiol-functionalized zirconium (UIO-66 topology) and aluminum (CAU-1 topology, CAU = Christian-Albrechts University) MOFs, which can selectively remove mercury from aqueous solutions—even from solutions with a very low concentration of mercury (~ 10 ppm).⁴³ The mercury uptake for an as-synthesized zirconium MOF was found to be ~ 182 mg g^{-1} under the experimental conditions. Remarkably, the uptake capacity remains very similar over a wide pH range, confirming the stability of the ion-exchange material. The Zr-MOF in its activated form shows a drop in mercury adsorption capacity because of the formation of an $-\text{S}-\text{S}-$ type disulfide bond which is not able to coordinate with an incoming mercury cation. This information also serves as an indirect proof (apart from infrared and Raman studies) that the primary bonding site of the incoming Hg^{2+} group is the $-\text{SH}$ group. The MOF can

also capture elemental mercury from the vapor phase (~ 12 wt%), further establishing the strong bonding interaction between the thiol group and the mercury atom.

Lin and coworkers investigated Zr-MOFs for their potential as uranium sorbents.⁴⁴ A diethoxyphosphorylurea functionalized zirconium-based MOF with UIO-68 architecture was prepared and tested for UO_2^{2+} capture from aqueous solution. Experimental and computational studies have shown that phosphorylurea moieties can preferentially adsorb actinides and lanthanides from acidic solution. Uranium sorption experiments were performed in water and simulated seawater at pH 2.5 and 5, followed by analysis of the supernatant by ultraviolet (UV) spectroscopy and inductively coupled plasma mass spectroscopy (ICP-MS). The MOF exhibited a saturation capacity of 217 mg U g^{-1} in water and 188 mg U g^{-1} in simulated seawater at pH 2.5, which decreased to 152 mg g^{-1} in water at pH 5. Density functional theory calculations were performed to understand the binding interaction of UO_2^{2+} species with phosphorylurea groups under experimental conditions.

Chen and coworkers recently reported a cationic zirconium MOF, ZJU-101, which can selectively remove $\text{Cr}_2\text{O}_7^{2-}$ from water.⁴⁵ ZJU-101 is synthesized from parent MOF-867 by post-synthetic modification (PSE) and contains a pendant N^+-CH_3 group on the aromatic side chain and anionic NO_3^- groups in the channel. Because of the presence of a cationic group, ZJU-101 shows far superior anionic removal efficiency than the parent MOF, reaching a maximal capacity of 245 mg g^{-1} . ZJU-101 retains its $\text{Cr}_2\text{O}_7^{2-}$ selectivity (capacity drop of $\sim 12\%$) in the presence of excess competing anions such as Cl^- , Br^- , NO_3^- , SO_4^{2-} , I^- , and F^- .

Apart from traditional ion-exchange processes in MOFs or coordination polymers, where extra-framework ions could be exchanged with ion-exchange solutions by ion diffusion, methods such as competitive crystallization, post-synthetic metal or linker exchange, and incorporation of targeted ions by direct bond formation have also been explored as a way to capture environmentally and industrially important ions on a non-elutable basis.^{4,40} In the case of competitive crystallization, the synthesis of MOFs (or coordination polymers) is carried out in solution containing the target ions (often a mixture of ions), and the resulting MOF includes one or more ions as a part of its structural motif. But as a non-elutable process, this method is not very economical, since the target ion becomes part of the structural motif as well. Recently, several reports have appeared in literature, notably from the Dinca and Cohen groups, on post-synthetic ligand and cation exchange in “robust” MOFs under relatively mild conditions.⁴⁶ In this process, an already synthesized MOF was immersed in a solution containing a metal ion (for metal exchange) or an organic linker (for linker exchange) of similar electronic and steric character and the exchange process was monitored by different types of physical techniques such as ICP, NMR, and powder XRD. Such a PSE process is important as it opens up new possibilities of preparing novel materials that cannot be obtained *via* other synthetic methods. For example, Dinca and coworkers showed that “inert” inorganic clusters in MOFs can be used to trap metal

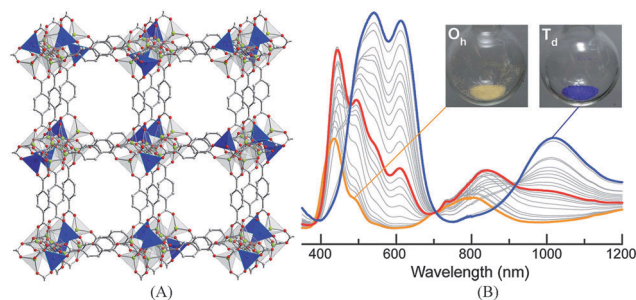


Fig. 10 (A) Part of the crystal structure of $\text{Ni}_x\text{Zn}_{4-x}\text{O}(\text{bdc})_3$ ($x = 1$). The position of the Ni^{2+} ion within the NiZn_3 clusters cannot be determined because of the crystallographic symmetry consideration; (color scheme: Ni: blue, Zn: green, O: red, C: gray). Hydrogen atoms are omitted for clarity. (B) *In situ* diffuse reflectance spectra depicting the color progression from yellow $\text{DMF}_2\text{Ni-MOF-5}$ to blue Ni-MOF-5 via a putative penta-coordinated Ni^{2+} intermediate. Reprinted with permission from ref. 47. Copyright 2012, Royal Society of Chemistry.

ions in coordination geometries that are difficult to achieve in molecular chemistry. In particular, the “inert” $\text{Zn}_4\text{O}(\text{COO})_6$ cluster acts as a tripodal chelating ligand for incoming Ni^{2+} ions, forming a pseudo-tetrahedral oxygen ligand field around it (Fig. 10).⁴⁷ Similarly, exchange of imidazole based organic linkers in ZIF-8 (ZIF = zeolitic imidazolate framework) has been shown under post-synthetic conditions.⁴⁶ These “post-synthetic” procedures have the potential to capture targeted ions from solution, although, similar to the competitive crystallization process, the process is non-elutable in nature. However, the method is often slow (*e.g.*, days or months in some cases) compared to traditional ion-exchange processes, and so far PSE is not envisioned as a replacement for traditional ion-exchange processes involving extra-framework ions. The third process, namely ion capture by bond formation, relies on the formation of permeant chemical bonds (ionic/covalent) with the MOF itself.⁴⁸ The MOFs in these cases are generally ionic in nature, where the charge balance is achieved by the uptake of extra-framework ions themselves. The difference between these MOFs and the ones discussed above (*e.g.*, by Stock and Lin, respectively) is that in the current case the MOF is ionic in nature and the cation (or anion) is added for charge balance, without any need for further functionalization. For example, we recently reported a soft anionic MOF, constructed from the flexible ionic linker tetrakis[4-(carboxyphenyl)oxamethyl]methane acid, that acts as a cation receptor *via* ligand-directed SC–SC structural transformation (Fig. 11).⁴⁸ The transformation is driven by the incorporation of divalent transition metal cations (*e.g.*, cobalt) in the free carboxylate groups of the organic ligand, thus transforming the anionic framework to a neutral and heterobimetallic system. The system works more like an “ion trap” than an ion exchanger, and thus differs considerably from the “post-synthetic modification” of MOFs described above. So far, there are a fairly large number of scientific reports regarding ion exchange in MOFs, involving both cations and anions, by different types of ion-exchange mechanisms. Although no direct study involving TcO_4^- has been reported in MOFs so far, several reports of environmentally pollutant oxoanion

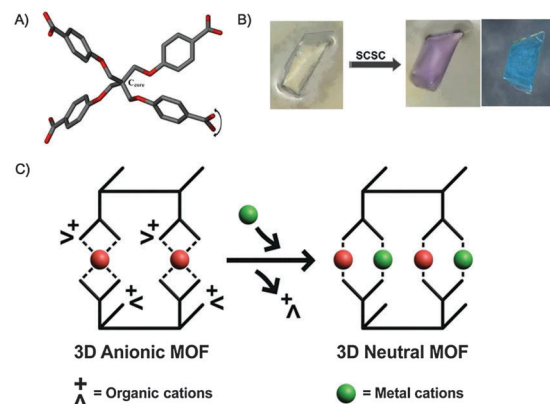


Fig. 11 (A) Structure of the semi-rigid carboxylate linker tetrakis[4-(carboxyphenyl)oxamethyl]methane acid (H4L) (color scheme: C: gray, O: red). Flexibility arises from twisting of the benzoate moieties around the central quaternary carbon atom (denoted as C_{core}) through ether links. (B) Photographs of crystals before and after TM^{2+} capture. (C) Scheme showing the incorporation of TM^{2+} cations into the anionic networks to afford neutral and heterobimetallic systems *via* ligand directing SC–SC structural rearrangement. Reprinted with permission from ref. 48. Copyright 2012, American Chemical Society.

(*e.g.*, CrO_4^{2-} , MnO_4^- , ClO_4^-) exchange using MOFs or coordination polymers are known.^{4,14,40,49–51} These oxoanions along with ReO_4^- are referred to as models to understand the TcO_4^- removal mechanism from low-dimensional coordination polymers or MOFs. For example, Oliver and coworkers have reported extensively on the removal of oxoanions (*e.g.*, CrO_4^{2-} , ClO_4^- , MnO_4^- , ReO_4^-) from aqueous solution using a number of cationic coordination polymers, such as $[\text{Zn}_x\text{Co}_{1-x}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2]^{2+}$ ($4,4'\text{-bipy} = 4,4'\text{-bipyridine}$).^{14,49–51} The material possesses a cationic layered structure, with a weakly bound α,ω -alkanedisulfonate anion present between the layers.⁴⁹ The intermellar α,ω -alkanedisulfonate anion can be exchanged with chromate, with a recorded adsorption capacity of 68.5 mg g^{-1} ($0.43 \text{ mol mol}^{-1}$) for $[\text{Zn}_{0.5}\text{Co}_{0.5}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2]^{2+}$. Interestingly, these materials are shown to be selective for CrO_4^{2-} in the presence of even a large excess of common competing anions such as nitrate and sulfates, indicating a “selective binding” of CrO_4^{2-} within the layer because of size and charge similarities with α,ω -alkanedisulfonate. The same group reported a copper based cationic inorganic material, $[\text{Cu}_4(\text{OH})_6][\text{O}_3\text{SCH}_2\text{CH}_2\text{SO}_3] \cdot 2\text{H}_2\text{O}$, which they call SLUG-26; it consists of a cationic copper hydroxide layer with 1,2-ethanedithiolate (EDS) as an interlamellar charge-balancing anion.⁵¹ The intercalated anion was readily exchanged with various α,ω -alkanedicarboxylate salts (*e.g.*, succinate) and permanganate, which was employed as a group-7 oxoanion model for pertechnetate; however, the process is not reversible. The total uptake capacity was $\sim 201 \text{ mg g}^{-1}$ after 48 hours as monitored by UV-Visible (UV-Vis) spectroscopy. Moreover, powder XRD on the samples before and after anion exchange confirmed that SLUG-26 retains its crystalline layered character, with *d*-spacing decreasing from 9.6 \AA to 7.4 \AA because of the smaller size of the MnO_4^- anion. Working on similar synthetic routes, the group reported a silver based coordination polymer (SLUG-21), which consists of cationic layers with π – π stacked chains of alternating metal and

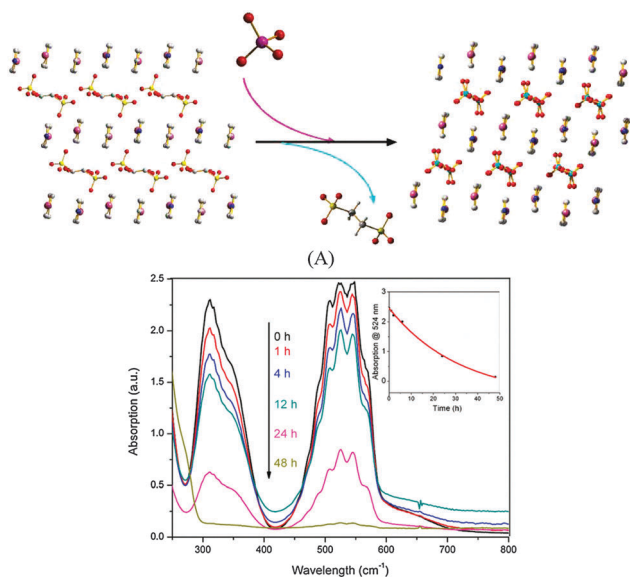


Fig. 12 (A) (left) Crystallographic view along the $[10\bar{1}]$ direction of the SLUG-21 structure; (right) crystallographic view along the $[01\bar{1}]$ direction of the crystal structure after perchlorate anion exchange (color scheme: Ag: purple; C: gray; S: yellow; O: red; N: blue; Cl: green; hydrogen atoms are omitted for clarity) (B) UV-Vis absorption spectra of the permanganate solution with an initial concentration of 6.33×10^{-5} mol in 50 mL solution and 3.17×10^{-5} mol SLUG-21 at various intervals; (inset: relative intensity of the 524 nm MnO_4^- maximum versus time). Reprinted with permission from ref. 14. Copyright 2011, American Chemical Society.

bipyridine linkers. The anionic template, EDS, was shown to be readily exchanged with oxoanions, such as MnO_4^- , ClO_4^- , and ReO_4^- , accompanied by a structural transformation of the host material, as evident from the powder XRD patterns of the exchanged material (Fig. 12).^{14,50} The ReO_4^- uptake capacity was calculated to be ~ 62 wt% after 48 h, much higher than the representative LDH material under similar experimental conditions. More importantly, SLUG-21 was shown to be selective toward oxoanions over common anions (e.g., NO_3^- , CO_3^{2-}) due to stability of the oxoanions in the resultant structure, and has the following order: $\text{MnO}_4^- > \text{ReO}_4^- > \text{ClO}_4^- > \text{CrO}_4^- > \text{NO}_3^- > \text{CO}_3^{2-}$.

As noted above, MOFs offer outstanding structural diversity and synthetic modularity that is absent in other traditional functional materials, but as most MOFs are neutral in nature, ion exchange is often overlooked as an important application. Moreover, i-MOFs are often found to be unstable under “real-world” exchange conditions and not specifically selective toward particular ions. However, with the advent of many ultra-stable MOFs (e.g., the UIO-series and the MIL-series, MIL = Material Institute Lavoisier), the scenario will likely change soon.

4. Conclusion and future outlook

There is an urgent need for development of TcO_4^- -selective materials, in light of the radioactivity and environmental mobility of TcO_4^- species. Several types of materials ranging

from molecular complexes to pure inorganics have been tested for TcO_4^- removal from solution. Among these materials, macromolecular hosts such as those based on cryptands and calixarenes show almost stoichiometric uptake of the guest TcO_4^- molecule, but the separation process is based on an inefficient, time-consuming solvent-extraction method, which is hard to implement from an engineering point of view. However, detailed structure–property knowledge regarding anion exchange has been established during many systematic studies involving molecular and supramolecular complexes, which was later implemented to impregnate specific functional groups (e.g., crown ether) on solid matrixes such as resins. Traditional solid-state materials, such as both natural and synthetic layered-hydroxide-type materials, have also been extensively tested, but showed a relatively low capacity and, more importantly, selectivity to TcO_4^- in the presence of other ions. Finally, in the last two decades, research oriented toward the synthesis and property evaluation of novel MOF materials has gained tremendous momentum because of their many unique properties, such as chemical tunability. Although to date, no traditional MOF-based materials have been tested directly for TcO_4^- (or ReO_4^-) ion exchange, several MOFs have been shown to have excellent exchange properties for larger oxyanions such as $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- . The enormous structural and chemical diversity of MOF-based materials and recent discoveries related to a number of ultra-stable, easy to synthesize MOFs will surely lead to more efforts toward assessing the TcO_4^- capacity and selectivity of these unique classes of materials for nuclear waste disposal in the near future.

Abbreviations

3D	Three dimensional
4,4'-bipy	4,4'-Bipyridine
ABEC	Aqueous biphasic extraction chromatography
CAU	Christian-Albrechts University
CTV	Cyclotrimeratylene
EDS	1,2-Ethanedisulfonate
HLW	High-level waste
ICP	Inductively coupled plasma
i-MOF	Ionic metal–organic framework
LAW	Low-activity waste
LDH	Layered double hydroxide
MAS	Magic-angle spinning
MIL	Material Institute Lavoisier
MOF	Metal–organic framework
NDTB	Notre Dame thorium borate
NMR	Nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
PBU	Primary building unit
PCP	Porous coordination polymer
POP	Porous organic polymer
PSE	Post-synthetic modification
SBU	Secondary building unit
SC	Single crystal

TM	Trademark
TREN	Tris(2-aminoethyl)amine
TTU	TRENtris-urea
UIO	University of Oslo
UV	Ultraviolet
XRD	X-ray diffraction
ZIF	Zeolitic imidazolate framework

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